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Infrared and Raman spectra, ab initio calculations and conformational studies of ethyl iodosilane

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Abstract

Ethyl iodosilane (CH₃CH₂–SiH₂I) was synthesized for the first time. Infrared spectra were recorded in the vapour, amorphous and crystalline solid phases in MIR and FIR regions. Additional MIR spectra of the compound isolated in argon and nitrogen matrices were obtained at 5 K. Raman spectra of the liquid, excited by argon and by Nd³⁺ YAG lasers, were recorded at room temperature including polarization measurements. The spectra were studied in an extended temperature range 173–353 K and a ΔH value of 1.2 ± 0.3 kJ mol⁻¹ was obtained with *gauche* being the low energy conformer. Spectra of the amorphous and crystalline solids were obtained at liquid nitrogen temperature. Ethyl iodosilane exists in an equilibrium between *anti* and *gauche* conformers, in the vapour, liquid and amorphous states. After careful annealing the amorphous solid on a cold Cu finger (Raman) or on a CsI or Si window (infrared) to 160 K a partly crystalline solid was formed. A number of IR and Raman bands were reduced in intensity after annealing, although they did not vanish completely. From comparison between the observed and calculated vibrational modes it was apparent that the *gauche* conformer was present in the crystal. The sample was mixed with argon and nitrogen in a ratio 1:1000, deposited on a window at 5 or 10 K and annealed to temperatures between 5 and 36 K (argon) and 5–30 K (nitrogen). IR bands attributed to the *anti* and *gauche* conformers were reduced and increased in intensities, respectively. Thus, the *gauche* conformer was the low energy conformer in the matrices and probably also in the vapour phase.

Ab initio calculations were performed at the RHF/3-21 G* and 6-311G* B3LYPs and gave optimized geometries, IR and Raman intensities and vibrational frequencies for the *anti* and *gauche* conformers. An enthalpy difference of 0.9 kJ mol⁻¹ was obtained from the calculations with *gauche* being the low energy conformer. After scaling, a reasonably good agreement between the experimental and calculated wavenumbers for the *anti* and *gauche* conformer was obtained. The spectra of ethyl iodosilane were closely related to those of the corresponding ethyl fluoro, ethyl chloro and ethyl bromosilane. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Infrared spectra; Ethyl iodosilane; Raman spectra; Matrix isolation spectroscopy; Conformations; Ab initio calculations

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1. Introduction

In our laboratories, a series of halogenated silanes, disilanes and trisilanes have been synthesized. They were investigated by infrared and Raman spectroscopy and some compounds have also been studied by gaseous electron diffraction. We are interested in comparing the thermodynamic and spectroscopic results for various halosilanes and the differences caused by the various halogen substituents. Various silanes with conformational equilibria containing one [1-3], two [4-7] and three [8,9] silicon atom have been investigated. It is of particular interest to compare the vibrational spectra and the conformational equilibria in molecules with C-C, Si-C and Si-Si central bonds, to elucidate the differences between the carbon and silicon atoms, the bonds and the barrier to internal rotation.

Ethyl iodosilane (CH₃CH₂–SiH₂I), later to be abbreviated EISI, was synthesized and the infrared and Raman spectra were investigated. Raman spectra of the liquid were recorded and polarization ratios were obtained. Raman spectra were recorded at different temperatures to obtain the enthalpy difference between the conformers. Raman spectra of EISI were recorded using both visible (argon laser, frequency doubled Nd³⁺YAG laser) and near IR laser (Nd³ + YAG), and spectra of the crystal, obtained by different cooling techniques, were observed.

The vapour, amorphous and crystalline samples of EISI were recorded in the middle (MIR) and far infrared (FIR) regions. Infrared matrix isolation technique was employed to obtain spectra of the compound trapped in argon and nitrogen matrices. With this technique, neighbouring bands of different conformers, which overlap in spectra of the vapour and liquid, can frequently be separated, due to the narrow band widths observed in the matrix spectra. Also, by appropriate annealing of the matrices in the temperature range 25-38 K, the conformational barriers can often be estimated in the matrices.

The conformational energies, the structure, the force constants and the Raman and infrared intensities were calculated by ab initio quantum chemical methods. Two staggered conformations of EISI are



Fig. 1. The anti and gauche conformers of ethyl iodosilane (EISI).

expected and are illustrated in Fig. 1. The spectra and conformations of EISI are very similar to those of the related compounds: ethyl fluorosilane [10], ethyl chlorosilane [11] and ethyl bromosilane [12] which have recently been studied. A preliminary account of the results for EISI and the related molecule ethyl diiodosilane has already been reported [13].

2. Experimental

2.1. Sample preparation

Halogenated silanes are sensitive towards moisture and, in the case of iodosilanes, also towards oxygen. All reactions and manipulations therefore were carried out in an inert atmosphere of nitrogen using standard Schlenk techniques. All solvents were distilled from potassium in a nitrogen atmosphere prior to use. The purities of the compounds were checked with ¹H and ²⁹Si-NMR spectroscopy (solutions in C₆D₆), elemental analysis as well as gas chromatography coupled with mass spectrometry.

Ethyliodosilane, EtSiH₂I (EISI) was prepared by protodearylation of ethylmesitylsilane (which in turn was prepared by reduction of ethylmesityldichlorosilane) with liquid hydrogen iodide in a sealed glass tube. 0.9 g (21.9 mmol) of EtMeSiH₂ or 4.5 g (21.2 mmol) of EtPh₂SiH was placed in a thick-walled glass tube. With the aid of a vacuum line, a tenfold excess of hydrogen iodide HI was then condensed into the tube which was then sealed *in vacuo*. The tube was kept at -35 °C for one week, then opened cautiously. The excess of hydrogen iodide was condensed off with the aid of a vacuum line and the liquid residue consisting of the desired iodosilane and mesitylene or benzene was fractionated. In this way, 3.76 g (20.2 mmol,

92%) of EISI was obtained as a colourless liquid; b.p._{760 mmHg} = 90–95 °C; ²⁹Si-NMR: $\delta = -40.4$ ppm against TMS, ¹J(SiH) = 266.6 Hz.

2.2. Infrared spectral measurements

The spectra in the MIR were recorded on the following Fourier transform spectrometers: a Bruker model IFS-88 (4000–450 cm⁻¹), a Bruker model 66 (4000–450 cm⁻¹) and a Perkin–Elmer model 2000 (4000–450 cm⁻¹). Spectra in the FIR were covered by a Bruker IFS-113v vacuum spectrometer (600– 50 cm⁻¹). Beamsplitters of Ge substrate on KBr were employed in the MIR, and beamsplitters with 3.5 and 12 μ m thickness of Mylar were used in the FIR. The vapour was studied in cells with KBr (10 cm) and polyethylene windows (20 cm) in MIR and FIR, respectively. The amorphous and crystalline solids were deposited on a CsI window in the MIR and on a wedge shaped window of silicon in the FIR; both cryostats were cooled with liquid nitrogen.

The sample was diluted with argon or nitrogen (1:1000) and deposited on a CsI window at 5 K of a Displex cryostat from APD (model HS-4) with a three stage cooling system. Independent matrix spectra were obtained with a closed cycle cryostat from Leybold (model RGD 210) deposited at 10 K, employing a similar technique. The spectra of the unannealed matrices were first recorded. Subsequently, the matrices were annealed to temperatures between 15 and 20 K to remove site effects. Then they were annealed in steps of 3-5 K to a maximum of 36 K in argon and 32 K in nitrogen, in periods from 10 min to 1 h. Higher temperature measurements are not feasible since the inert gases have too high a pressure in the cryostat and the matrices turn 'soft' followed by diffusion of the solute. After each annealing the window was recooled to 5 or 10 K and the spectra were recorded.

2.3. Raman spectral measurements

The Raman spectra of EISI were obtained on a single channel, triple monochromator spectrometer Dilor RTI-30 and on a multichannel Dilor XY 800 spectrometer, excited by argon ion lasers (Spectra-Physics model 2000 and Carl Zeiss, Jena Model ILA20-1), using the 514.5 µm line. An additional

spectrometer from Jobin Yvon was employed, using a frequency doubled Nd³⁺:YAG laser resulting in a green line at 532 µm. An FT-Raman spectrometer from Bruker was also used, excited by an Nd³⁺:YAG laser operating at 1.064 µm. The liquid was recorded in a capillary at room temperature using each of the four spectrometers and polarization measurements were made with argon laser excitation. The temperature dependent measurements were carried out with a device consisting of a copper block on which the capillary with the substance is mounted. The copper block was placed in an evacuated chamber equipped with quartz windows and is cooled with liquid nitrogen from a small Dewar vessel. It can also be heated resistively, and with a small thermocouple the temperature is monitored and controlled. Thus, temperatures above ambient were obtained using the same setup, and temperatures between 353 and 173 K were employed. Band areas were used in the van't Hoff plots and the convolutions were made with the Peakfit program package.

Spectra of the crystal were obtained in a capillary tube of 2 mm inner diameter surrounded by a Dewar, cooled by gaseous nitrogen evaporated from a reservoir [14]. Independently, the vapour of EISI was condensed on a copper finger at 78 K. An amorphous phase was first formed and after annealing to ca. 145–165 K and recooling to 78 K, a partly crystalline phase was obtained. The presence of a crystal was apparent from frequency shifts of the bands relative to the amorphous phase and sharpening of the bands. Certain bands belonging to the high energy conformer were reduced in intensity (but did not completely disappear). However, we did not observe any clear-cut cases of lattice modes in the low frequency region.

3. Results

3.1. Infrared spectral results

Infrared vapour spectra of EISI in the $1300-475 \text{ cm}^{-1}$ region are given in Fig. 2. A vapour spectrum in the region $600-80 \text{ cm}^{-1}$ at full pressure appears in Fig. 3. As is apparent from these figures, some bands had well resolved rotational fine structure



Fig. 2. MIR spectrum of EISI as a vapour in a cell with 10 cm path and full pressure (15 Torr) in the range 1300-475 cm⁻¹.

with possible A, B, C or hybrid structure as described in Table 1.

The infrared spectra of the amorphous and annealed solids at 78 K are presented in the regions $3000-2000 \text{ cm}^{-1}$ (Fig. 4), $1300-500 \text{ cm}^{-1}$ (Fig. 5) and the region (600-50) cm⁻¹ (Fig. 6). Some bands present in spectra of the amorphous solid (solid line) vanished or were reduced in intensities in the spectra of the crystal after annealing (dotted line): 1005, 900, 845, 763, 684, 427, 382 and 231 cm^{-1} . They are generally the same bands as those disappearing in the Raman spectra of the crystal (see below) and therefore belong to the high energy conformer of the liquid.

The infrared spectra of EISI in matrices at 5 or 10 K display much sharper bands than those recorded



Fig. 3. FIR spectra of EISI as a vapour in a cell with 20 cm path and pressure 15 Torr in the range 600-80 cm⁻¹.

in the vapour, liquid or crystalline states. They were recorded in argon and in nitrogen matrices at 5 or 10 K in the ratios (1:1000). Infrared spectra of EISI in unannealed nitrogen matrices and in matrices annealed to 32 K are given in Fig. 7 (1140- 800 cm^{-1}). Spectra in argon matrices have been omitted since it was observed that spectra of the annealed matrices in argon had considerably higher background than those recorded of the unannealed matrices. Much higher scattering from the annealed than the unannealed matrices has been observed also in various other halogenated silanes, making the interpretation more difficult [15,16]. In Fig. 7 the ordinate scale has been changed for the annealed matrices, making the curves more similar to those of the unannealed curves.

Supposedly, the conformational equilibrium of the vapour phase is maintained when the gas mixture is quickly frozen on the CsI window at 5 or 10 K, provided that the barrier to conformational equilibrium is high enough to prevent conversion. Small spectral changes occurred both in the argon and nitrogen matrices when the samples were annealed to temperatures below 20 K, indicating minor site effects in the matrices. At higher annealing temperatures (20-34 K) changes were observed both in the argon and nitrogen matrix spectra which were correlated with conformational changes in EISI.

It can be clearly seen from the observed spectra that the bands at 1006, 905, 839 and 806 cm⁻¹ (values in nitrogen) and those at 906, 852, 767, 688, 643, 555 and 408 cm⁻¹ (values in argon) are reduced in intensity after annealing. On the other hand the bands at: 1026, 987, 939, 873, 837, 818, 732, 648, 548 and 517 cm⁻¹ (nitrogen) and 1023, 978, 867, 765, 734, 682, 648, 517 and 412 cm⁻¹ (argon) are enhanced after annealing.

In most cases the bands being reduced in intensity in one or both matrices after annealing were the same as those being reduced in intensity after crystallization. Moreover, the bands being enhanced mostly corresponded with those remaining in the crystal. Accordingly, the same conformer which was present in the crystal was also the more stable conformer in the matrices and probably also in the vapour. The matrix bands which increase or decrease in intensities after annealing are marked with arrows pointing upwards or downwards in Table 1. The fact that

Table 1 Infrared and Raman spectral data for ethyl iodosilane, $CH_3CH_2SiH_2I\ (EISI)$

Infrared				Raman			Interpretation		
Vapour	Ar-matrix	N ₂ -matrix	Solid		Liquid	Amorphous	Crystalline	Anti	Gauche
298 K ^b	36 K ^a 5 K ^b	32 K ^a 5 K ^b	Amorphous 78 K ^b	Crystal 165 K ^a 78 K ^b	298 K ^b	78 K ^b	165 K ^a 78 K ^b		
3112 vw 3102 vw 3046 vw			3101 vw,br	3101 vw					
2977 s	2975 s								
2971 s	2970 s	2971 s	2956 vs	2959 s	2959 m, D?	2956 m	2954 m	$\mathbf{A}'' \boldsymbol{\nu}_1 \ \mathbf{A}' \boldsymbol{\nu}_1$	$\nu_1 \nu_2$
2931 m	2945 m	2945 m	2929 m	2931 m	2929 m, P	2930 m	2924 s	$A'' \nu_3$	
2920 vw, sh	2918 vw		2919 m,sh	2920 m	2918 vw, D	2920 m	2921 m		ν_3
2891 m	2894 w	2887 m, sh	2901 w	2905 vw	2904 m, P				ν_4
2885 m	2886 m	2885 m	2884 w 2870 s	2884 vw, sh (*) 2873 s	2882 s, P 2872 s, P	2883 m 2868 s	2882 m 2868 s	$egin{array}{ccc} \mathrm{A}' & u_4 \ \mathrm{A}' & u_5 \end{array}$	ν_5
2843 vw	2839 w		2850 vw	2850 vw	2850 vw				
2186 vs R	2196 vs	2197 s				2180 w, sh			
2183 vs Q	2190 vs	2188 vs	2179 vs	2175 vs	2180 m, D	2168 vs		$A'' \nu_6$	ν_6
2180 vs P	2186 vs								
2179 vs R									
2174 vs Q	2172 vs	2178 vs	2168 vs	2169 vs	2161 vvs, P	2163 vs		$A' \nu_7$	ν_7
2170 vs P	2167 w,sh	2168vw							
	2152 w,sh?	2152 w,sh?	2137 w,sh	2137 w,sh	2123 w, bd				
1471 w		1469 m	1465 vw		1464 w			$A'' \nu_8$	ν_8
1465 w Q 1458 w	1465 m	1462 m	1456 m	1456 m	1454 m, D	1454 w	1454 w	$A' \nu_9$	ν_9
1417 w	1419 w		1419 m	1419 m					
1412 w Q	1412 m	1411 m	1401 m	1401 m	1402 m, D	1401 w	1401 w	$\mathrm{A}' \nu_{10}$	ν_{10}
1407 w	1410 m								
1385 vw	1383 w 1245 m 1235 w	1383 m 1243 w	1368 w	1371 m	1377 w, P?	1378 w	1378 w	$A' \nu_{11}$	ν_{11}
1232 w Q	1232 w	1236 w↓	1231 m	1232 s	1226 s, P	1231 s	1231 w	$A'' \nu_{12}$	ν_{12}
1220 vw	1229 vw 1225 vw	1228 m↓	1222 s	1220 s	1223 w, sh, D	1222 m	1220 vvw	$A' \nu_{13}$	ν_{13}
1086 vw	1090 m,br	1075 m, br↓	1090 w 1070 w	1090 vw 1070vw					
1031 w R	1029 m↓	1027 m							
1028 w Q	1026 w †	1023 w↑	1025 s	1022 s	1022 w, P	1024 w	1024 w		ν_{14}
1023 w P	1023 w								
1013 m R		1010 m ↓							
	1007 s	1006 s l	1006 m↓	1005 vw (*)	1002 w.P		*	$A' \nu_{14}$	
1006 m P	981 w	983 w	987 w			986 vw, P		$A'' \nu_{15}$	
976 s Q	978 m↑	980 s	973 s, sh	975 s	972 vw,sh	976 m	974 m	10	ν_{15}
974 s	973 m	977 w							
969 s Q	970 s	969 s	965 vs	966 s	962 m, P	964 m	967 m		ν_{16}
964 s	957 m	959 w	954 w,sh	954 w,sh	- -				
	953 m							$A' \nu_{16}$	
946 s	947 s	944 s↓							
	945 s	939 s↓							

(continued on next page)

Table 1 (continued)

Infrared					Raman			Interpreta	tion
Vapour	Ar-matrix	N ₂ -matrix	Solid		Liquid	Amorphous	Crystalline	Anti	Gauche
	36 K ^a	32 K ^a	Amorphous	Crystal 165 K ^a	_		165 K ^a		
298 K ^b	$5 \ \mathrm{K}^{\mathrm{b}}$	5 K ^b	78 K ^b	78 K ^b	298 K ^b	78 K ^b	78 K ^b		
	943 s								
937 s	938 s	936 s	926 vs	928 vs	929 m, D	925 m	925 w	$A' \nu_{17}$	ν_{17}
	931 m 929 m	930 m↓							
900 vvw	906 m↓	905 w↓	898 w	900 w (*)					
882 m R	876 s	873 m ↓							
877 m P	867 s ↑	877 m	868 m	870 m					
852 w, sh	852 vw↓	854 vw	845 w	845 vvw (*)					
	838 vs	839 m↓							
		837 m †							
	832 vs	832 vw	829 m	828 m,sh					
827 vs R									
822 vs Q	819 vs	818 vs †	808 vs	804 vs	815 w	817 vw,sh	817 vvw		ν_{18}
817 vs P					804 w, br			. /	
806 m, sh	807 vs	806 vs ↓			797 w, br	802 w,br	802 vvw (*)	A' ν_{18}	
	791 vw	788 w							
774 W	779 vw	776	7(2	7(2) (*)	750	750	750 (*)	• //	
/68 W	/6/m	776 W	763 W	/63 VW()	759 VW	759 vvw	759 vvw()	$A'' \nu_{19}$	
729 a D	705 m 728 m	700 m 726 m l							
738 S K	730 III 734 m †	730 m ↓	720 10	720 m	726 m D	720 m	720 m		
733 S Q A	734 III 732 m	732 m j 721 m	129 8	729 III 725 o	720 III F	729 III	729 W		ν_{19}
720 51	700 yw	690 w		125 8					
	698 vw	070 W							
686 w	688 m l	686 w	685 m	*	677 m P	683 w	*	$A'\nu_{20}$	
679 w	682 m↑	683 m	684 m		0, , , , , , ,	000 11		11,20	ν_{20}
643 w	648 m	647 m	647 w. sh	643 m	637 vs. P	640 s	640 m		ν_{20}
639 w	643 w l	642 w	643 m	636 m	625 w. sh			$A'' \nu_{21}$	- 21
		622 vw			,			21	
	612 vw	613 vw							
			588 w		573 w,P				
	555 w↓								
	548 w↓								
535 m R	536 w			532 m					
530 m Q	532 w		531 s	523 s	527 w, P	532 m	532 w		ν_{22}
527 m Q									
523 m P	517 w↑		10.5		518 vvw?			. "	
486 w,sh	488 w		496 m	498 m		500 vvw	500 vvw	$A'' \nu_{22}$	
448 VW	120								
430 VW	439 m		126	427 yr (*)		424	125		
410 W	412 a t		420 VW	42/ VW ()		424 VVW?	423 VVW		
415 W	412 8 408 e								
400 w 392 m	400 S L		305 m	394 m	394 vvv	392 101	302 1000		
385 s			381 m	$382 \text{ w}(^*)$	377 ° P	377 w	372 vvw (*)	$\Delta' u_{\alpha\alpha}$	
359 s			501 III	502 w ()	577 5, 1	SITW	343 m sh	11 123	
355 s			338 vs	342 vs	340 vs. P	335 vs	335 vs		ν_{22}
349 s			200.0		2.0.0,1	000.0	200 10		- 23

Table 1 (continued)

Infrared					Raman			Interpretation	
Vapour	Ar-matrix	N ₂ -matrix	Solid		Liquid	Amorphous	Crystalline	Anti	Gauche
208 Kp	36 K ^a 5 <i>V</i> ^b	32 K ^a	Amorphous	Crystal 165 K ^a 78 K ^b	208 Kp	79 V ^b	165 K ^a 78 K ^b		
298 K	JK	JK	/0 K	/0 K	298 K	/0 K	/0 K		
270 w			275 m	279?	268 m P	274 m	274 m		ν_{24}
264 w									
233 w			231 vw	*;	228 s, P	229 w	*;	$A' \nu_{24}$	
225 w					215 vvw?	212 vw	212 vw		ν_{25}
					198 vw	190 vw	190 vvw*	$A'' \nu_{25}$	
138 vw					136 w, D	147 m, br	146 w		ν_{26}
				92 w					
115 vw					115 w, P			$A' \nu_{26}$	
			72 w	70 w		75 vw	74 vvw		
65 vw?				58 vw	60 vw	65 vw	61 vw	$\mathrm{A}''\nu_{27}$	ν_{27}

Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder, P, polarized; D, depolarized; P, Q, R, rotational fine structure; asterisks denote bands disappearing or diminishing in intensity in the crystal; $\downarrow \uparrow$ denote bands in the matrices with diminishing and increasing intensities, respectively, after annealing.

^a Annealing temperature.

^b Recording temperature.

the matrix bands never vanished after annealing suggests that the enthalpy difference in the matrices (and probably also in the vapour) was low. A new equilibrium was observed in the matrices in the range 5-34 K in which the conformational equilibrium was shifted in the direction of gauche after annealing compared to the equilibrium value in the vapour at room temperature. The fact that the intensity variations occur after annealing in the temperature range 28-34 K suggests that the barrier to internal rotation in EISI is approximately $8-10 \text{ kJ mol}^{-1}$, using the curves given by Barnes [17]. Some of the IR bands which change intensities after annealing have not been assigned to fundamentals, but are probably due to combination bands or overtones. In other cases matrix bands changing intensities were attributed to overlapping *anti* and *gauche* bands v_{12} , v_{13} and v_{15} .

3.2. Raman spectral results

Raman spectra of the liquid in the ranges 3000-2800 and 2600-50 cm⁻¹ are given in Fig. 8, and a spectrum of the annealed crystalline solid at 78 K is presented in Fig. 9. The following bands present in Raman spectra of the liquid and of the amorphous

solid disappear in the spectrum of the crystal: 1002, 759, 683 and 229 cm⁻¹. These bands are attributed to the second conformer which is absent in the crystal and are marked with asterisks in Table 1. In most cases the corresponding bands were also reduced in intensities in the infrared spectra after annealing.

By comparing with the calculated wavenumbers obtained from the ab initio calculations after



Fig. 4. MIR spectra of EISI in the range $3000-2000 \text{ cm}^{-1}$ at 78 K, solid curve, unannealed, amorphous solid; dashed curve, partly crystalline solid, annealed to 165 K.

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Fig. 5. MIR spectra of EISI in the range $1300-500 \text{ cm}^{-1}$ at 78 K, solid curve, unannealed amorphous solid; dashed curve partly crystalline solid, annealed to 165 K.

appropriate scaling, it will be shown below that the vanishing bands belong to the *anti* conformer. Accordingly, the bands present in the crystal should belong to the *gauche* rotamer. However, many of the fundamentals of one conformer overlap those of the other. The *anti* and *gauche* bands overlap more in silanes than in ethanes which is probably due to lower conformational barriers, relatively weak interaction between the end groups and the longer Si–C distance in the silanes compared to the C–C distance in ethanes.

The samples of EISI were slowly discolored by free iodine when irradiated with the 514.5 μ m radiation of an argon ion laser or the 532 μ m emission



Fig. 6. FIR spectra of EISI in the range $600-50 \text{ cm}^{-1}$ at 78 K, solid curve, unannealed amorphous solid; dashed curve partly crystalline solid, annealed to 165 K.



Fig. 7. MIR spectra of EISI in a nitrogen matrix (1:1000) recorded at 10 K, before annealing (solid line) and after annealing to 32 K (dashed line) in the region 1180-800 cm⁻¹.

from a frequency doubled Nd^{3+} :YAG laser. However, satisfactory Raman spectra with the argon laser line including polarization measurements were obtained with the multichannel spectrometer, requiring less exposure time. The spectra of the amorphous and crystalline solid and spectra in the low frequency range below 200 cm⁻¹ were observed with the triple monochromator of the Dilor instruments. Irradiation with the Nd³⁺:YAG laser at 1.064 µm did not give free iodine and good Raman spectra of the liquid were recorded with the FT technique above 200 cm⁻¹.

Variable temperature measurements of the liquid (353-173 K) revealed that some bands were reduced in intensity compared to neighbouring



Fig. 8. Raman spectra of EISI as a liquid at ambient temperature, excited by an argon ion laser.





Fig. 9. Raman spectra of EISI as a partly crystalline solid at 78 K, annealed to 165 K.

bands. This was interpreted as a displacement of the conformational anti-gauche equilibrium with temperature. The bands becoming weaker at low temperatures were the same as those vanishing or being reduced in intensities after crystallization, and to be discussed below these bands belonged undoubtedly to the anti conformer. The corresponding gauche bands were enhanced at low temperatures revealing that gauche was the low energy conformer. Among the conformer pairs observed, Raman pairs 677/727, 377/340 the and $228/268 \text{ cm}^{-1}$ were chosen, in which bands in the numerator belong to anti and those in the denominator to gauche. The intensities of each band pair were fitted to the equation: $-\ln K = \Delta H/RT -$ $\Delta S/R$ where K is the ratio of the integrated areas of



Fig. 10. Van't Hoff plot of the band pair $677*/726 \text{ cm}^{-1}$ in the temperature range 270-170 K.



Fig. 11. Van't Hoff plot of the band pair $377*/340 \text{ cm}^{-1}$ in the temperature range 353-192 K.

 I_{anti}/I_{gauche} , and it is assumed that the ΔH is constant with temperature. The data were plotted as van't Hoff plots in Figs. 10–12. The values obtained were 1.18, 1.22 and 1.33 kJ mol⁻¹ giving an average of 1.2 ± 0.3 kJ mol⁻¹ with gauche being the low energy conformer.

The observed infrared and Raman spectral data are listed in Table 1. As is apparent, Raman bands in the amorphous phase at 1002, 683, 377 and 229 cm⁻¹ vanished partly in the spectra of the crystal and have been marked with asterisks in Table 1. In spite of careful annealing the 'crystal phase' undoubtedly was mixed with amorphous material leading to incomplete disappearance of the high energy conformer bands. The same results were observed in the related ethyl bromosilane [12]. These partly vanishing bands in the spectra of EISI have been attributed to the high energy conformer which turned out to be *anti*.



Fig. 12. Van't Hoff plot of the band pair 228*/268 cm⁻¹ in the temperature range 353-173 K.

3.3. Quantum chemical calculations

HF, DFT (B3LYP) and MP2 calculations were carried out using the GAUSSIAN98 program [18] employing the 3-21G* and LanL2DZ basis sets. The minima on the potential surface were found by relaxing the geometry; the geometrical parameters obtained with the different methods were essentially identical and they are not presented here for the sake of brevity.

The calculations on EISI all favour *gauche* as the low energy conformer in agreement with the results for ethylfluoro- [10], ethylchloro- [11], and ethylbromosilane [12]. The differences between the calculated thermal corrections to the enthalpy for the *gauche* and *anti* conformations were negligible.

3.4. Normal coordinate calculations

Analytical H-F force constants were derived for each of the two conformers in EISI, using the MP2/LanL2DZ basis set. The calculated ab initio force constants were transformed from Cartesian to symmetry coordinates, derived from a set of valence coordinates. The ab initio calculated wavenumbers are invariably larger than the experimental values. In order to make a complete assignment of the observed infrared and Raman bands, a normal coordinate analysis with scaled force constants was carried out. Reasonably good agreement between the experimental and calculated wave numbers was achieved by using scaling factors of 0.95 for the stretching and bending modes above, and 1.0 for the modes below, 400 cm^{-1} . The infrared intensities, Raman scattering cross sections and Raman polarization ratios were calculated and the data are listed in Tables 2 and 3.

The potential energy distribution (PED) in Tables 2 and 3 is expressed in terms of the symmetry coordinates. The normalized symmetry coordinates are identical to those recently given in Ref. [13] for ethyl bromosilane and have been constructed from a set of valence coordinates. Only PED terms larger than 10% have been included in Tables 2 and 3 and the largest contribution described in terms of valence coordinates. The C–H and Si–F stretching modes are reasonably well localized, but the CH₃ rock, the C–C and C–Si stretches and the skeletal deformations are highly mixed. Obviously, the vibrational modes for the *anti* conformer, separated into symmetry species A' and A'' are more localized than those of the *gauche* conformer in which all the modes belong to the same species.

4. Discussion

4.1. Conformations

It can be seen from Table 1 that the vibrational bands at: 1010 (band center), 768, 686, 385 and 233 cm^{-1} (IR vapour bands) vanish or are reduced in intensity during crystallization both in the infrared and Raman spectra. In addition, the Raman bands at 797 and 573 cm⁻¹ and the infrared band at 900 cm⁻¹ seem to disappear in the crystal. Many of these bands also diminish in intensities after annealing in the IR spectra of the argon and nitrogen matrices.

Neither the infrared vapor contours, Raman polarization data nor the ab initio calculated energies could answer the following question: do the bands vanishing in the crystal spectra belong to the anti or the gauche conformer? While the calculated energies for the anti and gauche rotamers derived from the ab initio calculations have large uncertainties, the force constants and the wave numbers after appropriate scaling usually give a good agreement with those of the observed fundamentals. Within the group frequency regions for the CH₃ and CH₂ stretching and deformation vibrations, the calculated wave numbers for the anti and gauche fundamentals overlap nearly completely (Tables 2 and 3) except for ν_3 and ν_4 . Below 1200 cm^{-1} there are nine instances in which the *anti* and gauche fundamentals are separated more than 10 cm^{-1} , and in four cases (ν_{19} , ν_{22} , ν_{23} and ν_{24}) the shifts are larger than 30 cm^{-1} . Obviously, the observed anti/gauche band pairs are most likely to appear at these frequencies.

The following observed IR and/or Raman pairs (wavenumbers from IR spectra of the vapour, except for ν_{25}): 1006*/1028, 940/900*, 822/806*, 768*/733, 686*/679, 530/486*, 385*/355, 270/233* and 215/198* cm⁻¹. The bands with asterisks vanished in

 Table 2

 Observed and calculated normal modes of vibration in the gauche conformer of ethyl iodosilane (EISI)

No.	Freq. ^a	IR	R	ρ	Obs. ^b	PED ^c	Description
1	2971	32.5	25.1	0.61	2971	$30 S_1 + 64 S_{17}$	CH ₃ antisymmetric stretch
2	2967	42.5	53.2	0.64	2971	$68 S_1 + 26 S_{17}$	CH ₃ antisymmetric stretch
3	2939	2.2	94.8	0.75	2920	85 S ₁₈	CH ₂ antisymmetric stretch
4	2878	12.5	170.9	0.09	2891	91 S ₃	CH ₂ symmetric stretch
5	2871	39.9	78.1	0.05	2872 ^d	95 S ₂	CH ₃ symmetric stretch
6	2168	80.7	88.0	0.75	2183	100 S ₁₉	SiH ₂ antisymmetric stretch
7	2148	88.2	216.8	0.06	2174	100 S ₄	SiH ₂ symmetric stretch
8	1464	9.4	12.4	0.75	1471	$47 S_5 + 46 S_{20}$	CH ₃ antisymmetric deformation
9	1460	8.8	14.8	0.73	1465	$47 S_5 + 46 S_{20}$	CH ₃ antisymmetric deformation
10	1406	5.0	11.4	0.65	1412	90 S ₆	CH ₂ scissors
11	1391	7.9	2.0	0.68	1385	90 S ₇	CH ₃ symmetric deformation
12	1271	6.4	2.2	0.25	1232	79 S ₈	CH ₂ wag
13	1228	6.4	7.8	0.75	1220	59 S_{21} + 29 S_{22}	CH ₂ twist
14	1020	13.7	8.5	0.65	1028	56 S ₁₀	CH ₃ rock
15	994	72.9	3.2	0.74	976	36 S ₂₁ + 33 S ₂₂	CH ₃ rock
16	954	1.1	9.1	0.45	969	80 S ₉	C-C stretch
17	920	121.9	27.4	0.74	937	98 S ₁₁	SiH ₂ def
18	808	266.5	7.2	0.53	822	$63 S_{12} + 16 S_{22}$	SiH ₂ wag
19	726	48.2	10.7	0.45	733	$17 \ S_{12} + 19 \ S_{23} + 31 \ S_{24}$	CH ₂ rock
20	656	1.7	21.0	0.74	679	52 S ₂₃₊ 27 S ₂₄	SiH ₂ twist
21	623	3.5	20.0	0.46	643	63 S ₁₃	Si-C stretch
22	513	19.4	10.7	0.61	530	79 S ₂₅	SiH ₂ rock
23	308	18.3	18.6	0.27	355	65 S ₁₄	Si-I stretch
24	262	2.8	5.9	0.48	270	19 S ₁₄ + 54 S ₁₅	C-C-Si bend
25	225	0.7	1.1	0.28	225	$17 \text{ S}_{15} + 62 \text{ S}_{26}$	CH ₃ torsion
26	121	0.6	4.2	0.68	138	60 S ₁₆	C-Si-I bend
27	63	0.2	1.7	0.75	65	84 S ₂₇	SiH ₂ I tors

^a Frequencies from MP2/LanL2DZ calculations have been scaled by 0.95.

^b IR vapour phase values except when noted.

^c For definition of symmetry coordinates, see Ref. [1].

^d Raman liquid values.

the infrared and/or Raman spectra. In all cases the bands marked with asterisks were correlated with the *anti*, the other bands with the *gauche* rotamer. Particularly convincing were the band pairs 768*/733 (ν_{19}), 530/486* (ν_{22}), 385*/355 (ν_{23}) and 270/233* (ν_{24}) predicted from the MP2 calculations to give shifts: 51, 37, 46 and 37 cm⁻¹, respectively, compared to the experimental values: 41, 44, 30, and 34 cm⁻¹.

As reported above the intensity variations observed in the IR spectra of EISI in the argon and nitrogen matrices after annealing supported the assignments into *anti* and *gauche* conformers. In most cases arrows pointing upwards (signifying increased intensity after annealing) correspond with *gauche* fundamentals while arrows pointing downwards fit with *anti* bands. The energy difference between the conformers is low since an equilibrium is attained at the annealing temperatures of 32–37 K.

Thus, the *gauche* conformer remains in the crystal and is also the low energy conformer in the liquid and in the matrices. The same conclusion was drawn from the results of the ab initio calculations in which all the basis sets predicted the *gauche* conformer to have the lower energy. Also, in both the two related compounds ethyl chlorosilane [12] and ethyl bromosilane [13] *gauche* was the low energy conformer and was also present in the crystal.

4.2. Spectral assignments

The assignments of the infrared and Raman spectra of EISI to the *anti* and *gauche* conformers appear in

 Table 3

 Observed and calculated normal modes of vibration in the *anti* conformer of ethyl iodosilane (EISI)

No.	Freq. ^a	IR	R	ρ	Obs. ^b	PED ^c	Description
1	2967 A"	46.2	9.1	0.75	2971	57 S ₁₇ + 43 S ₁₈	CH ₃ antisymmetric stretch
2	2967 A'	36.6	98.2	0.57	2971	99 S ₁	CH ₃ antisymmetric stretch
3	2949 A"	1.7	86.9	0.75	2931	43 S ₁₇ + 57 S ₁₈	CH ₂ antisymmetric stretch
4	2897 A'	12.0	84.2	0.14	2885	99 S ₃	CH ₂ symmetric stretch
5	2868 A'	42.9	135.4	0.01	2872 ^d	100 S ₂	CH ₃ symmetric stretch
6	2169 A"	76.6	79.9	0.75	2183	100 S ₁₉	SiH ₂ antisymmetric stretch
7	2150 A'	77.4	202.1	0.05	2174	100 S ₄	SiH ₂ symmetric stretch
8	1462 A"	12.9	19.3	0.75	1471	93 S ₂₀	CH ₃ antisymmetric deformation
9	1459 A'	5.4	11.9	0.74	1465	93 S ₅	CH ₃ antisymmetric deformation
10	1415 A'	5.0	12.8	0.54	1412	95 S ₆	CH ₂ scissors
11	1390 A'	4.9	1.0	0.61	1385	94 S ₇	CH ₃ symmetric deformation
12	1270 A'	2.8	1.6	0.28	1232	80 S ₈	CH ₂ wag
13	1229 A"	1.1	8.0	0.75	1220	$61 S_{21} + 28 S_{22}$	CH ₂ twist
14	1012 A"	10.4	4.5	0.75	1006	44 S_{21} + 35 S_{22} + 16 S_{24}	CH ₃ rock
15	1006 A'	79.9	5.2	0.46	981	$17 S_8 + 66 S_{10}$	CH ₃ rock
16	945 A'	7.7	16.3	0.44	946	78 S ₉	C-C stretch
17	923 A'	115.9	24.8	0.69	937	90 S ₁₁	SiH ₂ deformation
18	796 A'	297.3	14.0	0.50	806	92 S ₁₂	SiH ₂ wag
19	775 A″	21.8	7.5	0.75	768	$34 S_{22} + 16 S_{23} + 38 S_{24}$	CH ₂ rock
20	652 A'	16.4	14.9	0.19	686	82 S ₁₃	Si-C stretch
21	622 A"	3.3	23.8	0.75	639	$70 S_{23} + 20 S_{24}$	SiH ₂ twist
22	478 A″	12.4	5.7	0.75	486	$15 S_{24} + 69 S_{25}$	SiH ₂ rock
23	352 A'	23.2	15.8	0.35	385	54 S_{14} + 31 S_{15}	Si-I stretch
24	217 A"	0.2	0.2	0.75	233	83 S ₂₆	CH ₃ torsion
25	212 A'	3.6	10.6	0.30	198 ^d	47 S_{14} + 39 S_{15}	C-C-Si bend
26	103 A'	1.3	6.3	0.70	115	$24 S_{15} + 71 S_{16}$	C-Si-I bend
27	59 A″	0.2	0.6	0.75	65	90 S ₂₇	SiH ₂ I torsion

^a Frequencies from MP2/LanL2DZ calculations have been scaled by 0.95.

^b IR vapour phase values except when noted.

^c For definition of symmetry coordinates, see Ref. [1].

^d Raman liquid values.

Tables 1–3. For the sake of similarity, the fundamentals of both the *anti* and *gauche* conformers have been numbered consecutively, instead of the conventional numbering of the modes in the *anti* conformer belonging to species A' before those of A''.

The five hydrogens belonging to the CH₃ and CH₂ groups should give rise to five C–H stretching fundamentals v_1-v_5 of each conformer in the range 2980–2870 cm⁻¹. Three of the *anti* and *gauche* fundamentals apparently overlap while v_3 and v_4 are split into two conformer pairs. With two Si–H bonds we expect two fundamentals around 2200 cm⁻¹ for each conformer. The out-of-phase and the in-phase Si– H stretches give rise to intense, prominent Q-branches at 2183 and 2174 cm⁻¹, respectively, both having well resolved R and P branches. As expected the in-phase mode is much stronger in Raman than the out-of-phase mode. Both fundamentals have overlapping *anti* and *gauche* bands as predicted from the calculations.

The CH₃ deformation and the CH₂ deformation, wagging and twisting modes ($\nu_8 - \nu_{13}$) are expected in the range 1470–1200 cm⁻¹. In agreement with the results of the calculations all these modes will have coinciding *anti* and *gauche* bands. As is apparent from Table 1 they are attributed to mostly medium intense IR and Raman bands in the expected range. The C–C stretching mode (mixed with CH₃ rock) ν_{14} is assigned to the Q-branch at 1028 cm⁻¹ (*gauche*) and the band center at 1009 cm⁻¹ of a band with B-contour (*anti*). The latter IR band diminished in intensity in the crystal and the Raman band vanished. Of the two CH₃ rocking modes, ν_{15} is tentatively attributed to the bands at 981 (*anti*) and 976 cm⁻¹ (*gauche*) and ν_{16} to the bands at 969 (*gauche*) and 946 cm⁻¹ (*anti*) although the latter lacks Raman components. The SiH₂ scissor (ν_{17}) was tentatively assigned to overlapping modes at 937 cm⁻¹.

All the modes $\nu_{18} - \nu_{26}$ have been assigned to *anti* and *gauche* pairs. The calculations give large splittings for most of these modes (as large as 46 cm⁻¹ for ν_{23}) except for ν_{20} and ν_{21} , in which the shifts were only 4 and 1 cm⁻¹, respectively. In the conformer pairs ν_{18} , ν_{19} and ν_{20} the *anti* components are reduced or vanish in the crystal, and the gauche component is enhanced and the anti reduced in intensity in the matrix spectra after annealing. In the conformer pairs ν_{21} and ν_{22} , the crystal data are not conclusive, but at least in ν_{21}

the matrix data support the assignments. For both the modes ν_{23} , involving predominantly Si–I stretch, and ν_{24} (CH₃ torsion) the crystal data are conclusive and these pairs were employed for two of the van't Hoff plots (Figs. 11 and 12). The assignments of ν_{25} and ν_{26} are tentative, since the IR and Raman bands are weak and no matrix spectra were available in this low frequency range. Finally, the SiH₂I torsion (ν_{27}) is tentatively assigned to the IR and Raman bands around 65 cm⁻¹ for both conformers.

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The fundamental frequencies assigned to the more stable *gauche* conformer in EISI are compared with the corresponding fundamentals in the two related compounds ethyl chlorosilane [11] and ethyl bromosilane [12] in Table 4. It appears that most of

Table 4 Observed frequencies (cm^{-1}) for the *gauche* conformer of ethyl halosilanes (X = Cl, Br, I) in the vapour phase

Vib. No.	Fundamental	$X = Cl^a$	$X = Br^b$	$X = I^c$
ν_1	CH ₃ antisymmetric stretch	2979	2978	2971
ν_2	CH ₃ antisymmetric stretch	2972	2978	2971
ν_3	CH ₂ antisymmetric stretch	2928	2940	2920
ν_4	CH ₂ symmetric stretch	2905	2896	2891
ν_5	CH ₃ symmetric stretch	2885	2892	2872 ^d
ν_6	SiH ₂ antisymmetric stretch	2186	2187	2183
ν_7	SiH ₂ symmetric stretch	2180	2179	2174
ν_8	CH ₃ antisymmetric deformation	1468	1466	1471
ν_9	CH ₃ antisymmetric deformation	1458	1466	1465
ν_{10}	CH ₂ symmetric deformation	1411	1415	1412
ν_{11}	CH ₃ symmetric deformation	1392	1387	1385
ν_{12}	CH_2 wag	1242	1235	1232
ν_{13}	CH ₂ twist	1234	1225	1220
ν_{14}	C–C stretch	1031	1028	1028
ν_{15}	CH ₃ rock	972	978	976
ν_{16}	CH ₃ rock	981	970	969
ν_{17}	SiH ₂ deformation	952	950	937
ν_{18}	SiH ₂ wag	862	843	822
ν_{19}	CH ₂ rock	744	736	733
ν_{20}	SiH ₂ twist	693	662	679
ν_{21}	C-Si stretch	657	645	643
ν_{22}	SiH ₂ rock	562	549	530
ν_{23}	Si-X stretch	522	414	355
ν_{24}	CCSi bend/CSiX	283	276	270
ν_{25}	CH ₃ torsion	202	222 ^d	225
ν_{26}	CSiX bend/CCSi	158	140	138
ν_{27}	SiH2X/CCSi torsion	83	76 ^d	65

^a See Ref. [11]

^b See Ref. [12]

^c This work.

^d Frequencies from Raman spectrum of the liquid.

the vibrational modes do not vary much between the three compounds. An exception is v_{23} involving predominantly SiX stretch and to some extent ν_{26} CSiX bend/CSi bend which obviously are strongly depending upon the mass of the halogen. Since the SiX stretch and bend make contributions to many modes, it is expected that most modes are displaced towards lower wavenumbers going from Cl to Br to I. The Si-I stretch ν_{23} agrees well with earlier results for 1,2diiodosilane, 1,1,2,2-tetraiodosilane [19] and 1,1,2triiodosilane [5]. Furthermore, with a few exceptions the same low frequency vibrational modes $v_{17} - v_{26}$ form conformer band pairs in the three compounds [5, 19]. The enthalpy difference between the two conformers were 0.65 \pm 0.19 for ethyl fluorosilane [10], 0.93 ± 0.13 for ethyl chlorosilane [11] and 1.67 ± 0.3 kJ mol⁻¹ for ethyl bromosilane [12] compared with 1.24 \pm 0.3 kJ mol⁻¹ for EISI.

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